ALKOXYSILACYCLOALKANES, PROCESS FOR THEIR PREPARATION AND THEIR USE FOR THE POLYMERIZATION OF OLEFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. Application Serial No. 08/715,915, filed September 19, 1996, and also a continuation-in-part of U.S. Application Serial No. 09/572,372, filed May 5, 1999. U.S. Application Serial No. 08/715,915, filed September 19, 1996, and U.S. Application Serial No. 09/572,372, filed May 5, 1999 are hereby incorporated herein by reference.

ALKOXYSILACYCLOALKANES, PROCESS FOR THEIR PREPARATION
AND THEIR USE FOR THE POLYMERIZATION OF OLEFINS

FIELD OF THE INVENTION

The invention relates to alkoxysilacycloalkanes, to the

process for their preparation and to their use as electron-donor

in processes for the polymerization or copolymerization of

olefins like propylene or ethylene.

BACKGROUND OF THE INVENTION

A polyolefin which has an excessively high content of

heptane-solubles may have a tendency to stick and is therefore

difficult to convey and, as a result, is not very suitable for

industrial applications. In addition, in the alimentary field,

the presence of solubles in a polyolefin which is intended to

come into contact with foodstuffs is deemed to be undesirable.

For these reasons, for example, isotactic polypropylene

preferably has a heptane-insolubles content (denoted by HI, from

the expression "heptane-insoluble") higher than 80% by weight.

Patent Application EP 250229 teaches that the use of

certain silanes during the polymerization of olefins allows the

hexane-solubles content of the polyolefin obtained to be

reduced.

The paper by R. West, Journal of the American

Chemical Society (1954) 76, 6012, describes a method

for the preparation of 1,1-dimethoxysilacyclohexane.

This preparation involves numerous stages and the

5   intermediate formation of a chlorosilacycloalkane which

is particularly tricky to handle and easily degradable.

The process of the present invention is

particularly simple, involves raw materials which are

easily available and relatively stable and does not

10   involve any chlorosilacycloalkane. The stability of the

materials used reduces the risk of side reactions,

thereby tending in the direction of better purity of

the products which are finally prepared.

The presence of alkoxysilacycloalkanes in the

15   environment for the polymerization or copolymerization

of at least one olefin is reflected in an appreciable

increase in the polyolefin yield and in an appreciable

increase in the HI of the said polyolefin. In addition,

the alkoxysilacycloalkane acts as a morphology

20   protector in the suspension and gas-phase

polymerization or copolymerization processes. This

means that, in the case of these so-called

heterogeneous processes, the polymer or copolymer

formed is a better morphological replica of the initial

25   solid catalytic component if an alkoxysilacycloalkane

is introduced as an external electron-donor into the

polymerization or copolymerization environment.

The process according to the invention

includes the stage of reaction between an

5   alkylenedimagnesium dibromide of formula Br-Mg-A-Mg-Br

in which A is a divalent alkylene radical optionally

substituted, for example by an alkyl radical

containing, for example, from 1 to 6 carbon atoms, the

said alkylene radical containing from 4 to 7 carbon

10   atoms, the optional substituent(s) being excluded, and

a tetraalkoxysilane of formula $(OR^1)(OR^2)(OR^3)(OR^4)Si$ in

which R^1, R^2, R^3 and R^4, which may be identical or

different, denote linear or branched, saturated and/or

unsaturated hydrocarbon radicals which may include a

15   ring.

The radicals R^1, R^2, R^3 and R^4 preferably are

alkyl radicals containing from 1 to 6 carbon atoms.

The reaction may be carried out in a solvent

which preferably exhibits a Lewis base character, as is

20   the case with ethers. The solvent may, for example, be

diethyl ether.

The quantity of inert solvent which is

employed may, for example, be such that, assuming the

reaction yield to be equal to 100 %, the

alkoxysilacycloalkane formed is encountered again in a

concentration of between 0.05 and 2 moles/liter.

The reaction may be carried out, for example,

between 0 and 50°C for 10 min to 12 hours, if

5 appropriate under pressure if the volatility of the

species used makes this necessary, bearing in mind the

temperature chosen. Since the reaction is generally

exothermic, it is preferable to bring the dibromide and

the tetraalkoxysilane into contact gradually and with

10 stirring so as to retain control of the temperature of

the mixture. The reaction results in the formation of

at least one alkoxysilacycloalkane of formula

$$A \underset{\quad}{\overset{\quad}{\bigcirc}} Si \begin{array}{c} OX \\ OY \end{array} \qquad (I)$$
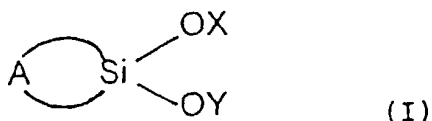
15

in which X and Y denote groups forming part of the

group of the radicals R^1, R^2, R^3 and R^4 and in which A

retains the meaning given above. The ring of the

alkoxysilacycloalkane therefore contains a silicon atom

20 and a number of carbon atoms equal to the number of

carbon atoms which the alkylene radical A contained,

the optional substituents of the said alkylene radical

being excluded.

The alkoxysilacycloalkanes in the case of which A is an alkylene radical containing at least one alkyl substituent are also a subject-matter of the present invention.

5   By way of example, Table 1 below mentions some alkoxysilacycloalkanes which can be prepared by the process according to the invention, by reaction of tetramethoxysilane with an alkylenedimagnesium dibromide, depending on the nature of the divalent

10   alkylene radical A included in the alkylenedimagnesium dibromide.

Nature of A	Alkoxysilacycloalkane formed
tetramethylene	1,1-dimethoxysilacyclopentane
1-methyltetramethylene	1,1-dimethoxy-2-methylsilacyclopentane
1-ethyltetramethylene	1,1-dimethoxy-2-ethylsilacyclopentane
1-n-propyltetramethylene	1,1-dimethoxy-2-n-propylsilacyclopentane
1-isopropyltetramethylene	1,1-dimethoxy-2-isopropylsilacyclopentane
1-n-butyltetramethylene	1,1-dimethoxy-2-n-butylsilacyclopentane
pentamethylene	1,1-dimethoxysilacyclohexane
1-methylpentamethylene	1,1-dimethoxy-2-methylsilacyclohexane
1-ethylpentamethylene	1,1-dimethoxy-2-ethylsilacyclohexane
1-n-propylpentamethylene	1,1-dimethoxy-2-n-propylsilacyclohexane
1-isopropylpentamethylene	1,1-dimethoxy-2-isopropylsilacyclohexane
1-n-butylpentamethylene	1,1-dimethoxy-2-n-butylsilacyclohexane
2,3-dimethyltetramethylene	1,1-dimethoxy-3,4-dimethylsilacyclopentane
1,4-dimethyltetramethylene	1,1-dimethoxy-2,5-dimethylsilacyclopentane
hexamethylene	1,1-dimethoxysilacycloheptane

<u>Table 1</u>

5   The reaction also gives rise to the formation

of BrMgOZ in which Z is a radical forming part of the

group of the radicals R^1, R^2, R^3 and R^4. This BrMgOZ,

considered as being a by-product in the context of the

present invention, is generally solid and can, in this

10 case, be removed, for example by filtration. After

evaporation of the optional solvent employed and of any excess reactants, the alkoxysilacycloalkane may be purified by distillation, preferably at reduced pressure, for example between 1 and 1×10^3 mbar.

5   The alkylenedimagnesium dibromide of formula Br-Mg-A-Mg-Br may be prepared, for example, by reaction between a dibromoalkane of formula Br-A-Br and magnesium in the presence of a solvent, for example an ether like diethyl ether, for example between 0 and

10   50°C, if appropriate under pressure if the volatility of the species used demands this, bearing in mind the temperature chosen.

The alkoxysilacycloalkanes capable of being obtained by the process according to the invention may

15   be used as an electron-donor in the polymerization or copolymerization of at least one olefin. For example, the silacycloalkane may be introduced within a solid catalytic component of the Ziegler-Natta type and may act as an internal electron-donor.

20   It is also possible to employ it as an external electron-donor in an environment for the polymerization or copolymerization of at least one olefin, so as to reduce the hexane-solubles content of the polymer or copolymer finally prepared.

In the case of this latter application (external electron-donor) it is preferred to employ an alkoxysilacycloalkane of formula (I) in which X and Y denote methyl radicals.

5   The alkoxysilacycloalkane preferably contains at least one alkyl substituent positioned alpha to the silicon atom. Particularly high HI values are obtained when the alkyl substituent contains at least two carbon atoms. An excellent compromise of properties (very high

10 HI and generally high yield) is obtained when the alkyl substituent contains 2 or 3 carbon atoms, as is the case with 1,1-dimethoxy-2-ethylsilacyclopentane, 1,1-dimethoxy-2-n-propylsilacyclopentane, 1,1-dimethoxy-2-isopropylsilacyclopentane, 1,1-dimethoxy-2-

15 ethylsilacyclohexane, 1,1-dimethoxy-2-n-propylsilacyclohexane and 1,1-dimethoxy-2-isopropylsilacyclohexane.

In accordance with a specific aspect of the present invention there is provided a process for

polymerizing at least one olefin in the presence of a catalyst and of a dialkoxysilacyclohexane of the formula

$$
\begin{array}{c}
R^1 \\
\diagdown \\
\text{Si} \diagup \text{OX} \\
\diagdown \text{OY} \\
R^2
\end{array}
\qquad (1)
$$

5
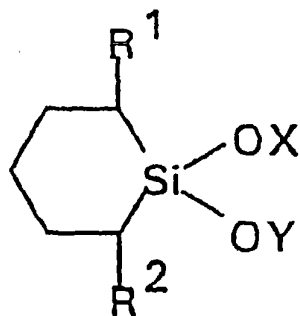
in which R^1 and R^2, which may be identical or different, represent alkyl radicals containing 1 to 5 carbon atoms, and X and Y, which may be identical or different, are alkyl radicals containing 1 to 6 carbon

10 atoms. R^1, R^2, X and Y may be selected from the radicals methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl and isobutyl. Preferably, at least one radical among R^1 and R^2 is an ethyl radical. More preferably still, R^1 and R^2 are both ethyl radicals.

15   The Applicant has found that the presence of the dialkoxysilacyclohexane of formula (1) in the polymerization medium resulted in a polymer having a higher heptane insolubility index coupled with, in general, a greater productivity, in comparison with an

20 identical process in which the dialkoxysilacyclohexane was replaced by the same number of moles of a dialkoxysilacyclohexane of identical structure but in

which at least one of the radicals R^1 and R^2 was

replaced by a hydrogen atom.

The following dialkoxysilacyclohexanes may be

used:

5   - 1,1-dimethoxy-2,6-dimethylsilacyclohexane,

- 1,1-dimethoxy-2,6-diethylsilacyclohexane,

- 1,1-dimethoxy-2,6-di-n-propylsilacyclohexane,

- 1,1-dimethoxy-2,6-diisopropylsilacyclohexane,

- 1,1-dimethoxy-2,6-di-n-butylsilacyclohexane,

10 - 1,1-dimethoxy-2-ethyl-6-methylsilacyclohexane,

- 1,1-dimethoxy-2-ethyl-6-n-propylsilacyclohexane,

- 1,1-dimethoxy-2-ethyl-6-isopropylsilacyclohexane,

- 1,1-dimethoxy-2-n-butyl-6-ethylsilacyclohexane,

- 1,1-diethoxy-2,6-dimethylsilacyclohexane,

15 - 1,1-diethoxy-2,6-diethylsilacyclohexane,

- 1,1-diethoxy-2,6-di-n-propylsilacyclohexane,

- 1,1-diethoxy-2,6-diisopropylsilacyclohexane,

- 1,1-diethoxy-2,6-di-n-butylsilacyclohexane,

- 1,1-diethoxy-2-ethyl-6-methylsilacyclohexane,

20 - 1,1-diethoxy-2-ethyl-6-n-propylsilacyclohexane,

- 1,1-diethoxy-2-ethyl-6-isopropylsilacyclohexane, and

- 1,1-diethoxy-2-n-butyl-6-ethylsilacyclohexane.

1,1-Dimethoxy-2,6-diethylsilacyclohexane is

particularly preferred.

25   The dialkoxysilacyclohexane acts as an

electron donor during the polymerization. When the

catalyst comprises a solid catalytic component, of the

Ziegler-Natta type, for example, the
dialkoxysilacyclohexane may be incorporated inside the
said solid component and be able to act as an internal
electron donor.

5   It is also possible to have the
dialkoxysilacyclohexane act as an external electron
donor in order to reduce the proportion of heptane
solubles in the polymer finally prepared. In this
latter case, the dialkoxysilacyclohexane may be
10   introduced into the polymerization medium independently
of the solid catalytic component. When the catalyst
system involves a solid catalytic component and a
cocatalyst, it is also possible to effect precontact
between the solid catalytic component, the catalyst and
15   the dialkoxysilacyclohexane before entry into the
polymerization medium.

The alkoxysilacycloalkane is generally
introduced in a proportion of 1×10^{-4} to 0.2 millimoles
20   per mole of olefin to be polymerized or copolymerized.
If the alkoxysilacycloalkane has been prepared in the
presence of a solvent of basic character in the Lewis
sense, it is recommended to remove the latter before
the polymerization or copolymerization stage because it

may have an undesirable influence on the structure of

the polymers formed. On the other hand, the

alkoxysilacycloalkane may be introduced in the

presence, for example, of an aliphatic, alicyclic or

5   aromatic hydrocarbon solvent which is not obviously of

a basic nature in the Lewis sense, like hexane,

cyclohexane or toluene.

A solid catalytic component containing a

transition metal is generally introduced into the

10   polymerization or copolymerization environment.

The transition metal may be chosen from the

elements of groups 3b, 4b, 5b, 6b, 7b and 8,

lanthanides and actinides, of the Periodic

Classification of the elements, as defined in the

15   Handbook of Chemistry and Physics, sixty-first edition,

1980-1981. These transition metals are preferably

chosen from titanium, vanadium, hafnium, zirconium and

chromium.

The solid catalytic component may be of the

20   Ziegler-Natta type and may, for example, be in the form

of a complex containing at least the elements Mg, Ti

and Cl, the titanium being in the Ti^{IV} and/or Ti^{III}

chlorinated form. The solid component may include an

electron-donor or acceptor.

A catalytic component of the Ziegler-Natta type is usually the result of the combination of at least one titanium compound, a compound of magnesium and chlorine and optionally an aluminium compound

5 and/or an electron-donor or acceptor, as well as any other compound that can be employed in a component of this type.

The titanium compound is usually chosen from the titanium chlorine compounds of formula $Ti-(OR')_xCl_{4-x}$

10 in which R' denotes an aliphatic or aromatic hydrocarbon radical containing from one to fourteen carbon atoms or denotes COR^5 with R^5 denoting an aliphatic or aromatic hydrocarbon radical containing from one to fourteen carbon atoms, and x denotes an

15 integer ranging from 0 to 3.

The magnesium compound is usually chosen from the compounds of formula $Mg(OR^6)_nCl_{2-n}$, in which R^6 denotes hydrogen or a linear or cyclic hydrocarbon radical and n denotes an integer ranging from 0 to 2.

20 The chlorine present in the component of Ziegler-Natta type may originate directly from the titanium halide and/or the magnesium halide. It may also originate from an independent chlorinating agent such as hydrochloric acid or an organic halide like

25 butyl chloride.

Depending on the nature of the transition metal included in the solid catalytic component, it may be necessary to add to the polymerization environment a cocatalyst capable of activating the transition metal of the solid component. The catalyst of the polymerization process according to the invention may therefore be a multi-component catalyst system, such as the combination of a solid catalytic component and a cocatalyst. If the transition metal is titanium, the cocatalyst may be chosen from organic aluminium derivatives.
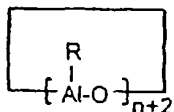
This organic aluminium derivative may be a derivative of formula $R^7R^8R^9Al$ in which each of R^7, R^8 and R^9, which may be identical or different, denotes either a hydrogen atom or a halogen atom or an alkyl group containing from 1 to 20 carbon atoms, at least one of R^7, R^8 and R^9 denoting an alkyl group. As an example of suitable compound there may be mentioned ethylaluminium dichloride or dibromide or dihydride, isobutylaluminium dichloride or dibromide or dihydride, diethylaluminium chloride or bromide or hydride, di-n-propylaluminium chloride or bromide or hydride, and diisobutylaluminium chloride or bromide or hydride. A trialkylaluminium such as tri-n-hexylaluminium, triisobutylaluminium, trimethylaluminium and triethylaluminium is employed in preference to the abovementioned compounds.

The cocatalyst may also be an aluminoxane. This aluminoxane may be linear, of formula

$$R_2\,Al\text{-}O\text{-}(Al\text{-}O)_n\text{-}Al\,R_2 \overset{\displaystyle R}{\underset{\displaystyle |}{}}$$, or cyclic, of formula

$$\left[\overset{\displaystyle R}{\underset{\displaystyle |}{\{Al\text{-}O\}}} \right]_{n+2}$$

R denoting an alkyl radical containing from one to six

carbon atoms and n being an integer ranging from 2 to

5 40, preferably from 10 to 20. The aluminoxane may

include groups R of different nature. All the groups R

preferably denote methyl groups. Furthermore, a

cocatalyst is also intended to mean mixtures of the

abovementioned compounds.

10   The quantities of cocatalyst which are

employed must be sufficient to activate the transition

metal. In general, when an organic aluminium derivative

is employed as cocatalyst, a quantity thereof is

introduced such that the atomic ratio of the aluminium

15 contributed by the cocatalyst to the transition

metal(s) which it is desired to activate ranges from

0.5 to 10 000 and preferably from 1 to 1000.

        The polymerization or copolymerization

process may be conducted in suspension, in solution, in

20 gaseous phase or in bulk.

A bulk polymerization process consists in performing a polymerization in at least one of the olefins to be polymerized which is kept in the liquid or supercritical state.

5   The solution or suspension polymerization processes consist in performing a polymerization in solution or in suspension in an inert medium and especially in an aliphatic hydrocarbon.

In the case of a solution polymerization

10   process it is possible to employ, for example, a hydrocarbon containing from eight to twelve carbon atoms or a mixture of these hydrocarbons. In the case of a suspension polymerization process it is possible to employ, for example, n-heptane, n-hexane,

15   isohexane, isopentane or isobutane.

The operating conditions for these bulk, solution, suspension or gas-phase polymerization processes are those that are usually proposed for similar cases making use of conventional catalyst

20   systems of the Ziegler-Natta type, whether supported or unsupported.

For example, in the case of a suspension or solution polymerization process it is possible to operate at temperatures ranging up to 250°C and at

pressures ranging from atmospheric pressure to
250 bars. In the case of a polymerization process in
liquid propylene medium the temperatures may range up
to the critical temperature and the pressures may be

5   included between the atmospheric pressure and the
critical pressure. In the case of a bulk polymerization
process resulting in polyethylenes or in copolymers in
which ethylene predominates it is possible to operate
at temperatures of between 130°C and 350°C and at

10   pressures ranging from 200 to 3500 bars.

A gas-phase polymerization process may be
employed using any reactor which permits gas-phase
polymerization, and in particular in an agitated-
bed (e.g. stirred) and/or a fluidized-bed reactor.

15   The conditions for implementing the gas-phase
polymerization, especially temperature, pressure,
injection of the olefin or of the olefins into the
reactor containing a stirred bed and/or a fluidized
bed, and control of the polymerization temperature and

20   pressure, are similar to those proposed in the prior
art for the gas-phase polymerization of olefins. The
operation is generally carried out at a temperature
that is lower than the melting point Tm of the polymer
prepolymer to be synthesized, and more particularly

between +20°C and (Tm-5)°C, and at a pressure such that

the olefin or the olefins are essentially in the vapour

phase.

The solution, suspension, bulk or gas-phase

5 polymerization processes may involve a chain transfer

agent, so as to control the melt index of the polymer

to be produced. The chain transfer agent employed may

be hydrogen, which is introduced in a quantity that can

range up to 90 % and preferably lies between 0.01 and

10 60 mol% of the combined olefin and hydrogen delivered

to the reactor.

The olefins that can be employed for the

polymerization or copolymerization are, for example,

the olefins containing from two to twenty carbon atoms

15 and in particular the alpha-olefins of this group.

Olefins which may be mentioned are ethylene, propylene,

1-butene, 4-methyl-1-pentene, 1-octene, 1-hexene, 3-

methyl-1-pentene, 3-methyl-1-butene, 1-decene, 1-

tetradecene or mixtures thereof.

20 The polymerization or copolymerization

process according to the invention is particularly

suitable for reducing the heptane-solubles content of

polymers or copolymers when the polymerization or

copolymerization environment includes an olefin

containing at least three carbon atoms. This process is therefore particularly suited for the polymerization or copolymerization of propylene.

In the examples which follow the heptane-insolubles content (represented by HI) was measured by extraction of the soluble fraction from the polymer using boiling heptane for two hours in an apparatus of the Kumagawa type.

Examples 1 to 15

a) Preparation of alkylenedimagnesium dibromides

In a 500-ml glass round bottom flask fitted with a water condenser, a thermometer and a mechanical stirring system and which has been purged with argon 0.2 moles of dibromoalkane of formula Br-A-Br in the form of a solution in 200 ml of anhydrous diethyl ether are added to 0.46 moles of magnesium, and this preparation is left stirred for 6 hours at ambient temperature. The preparation is then transferred to a dropping funnel.

b) Preparation of dimethoxysilacycloalkanes.

In a 1.5-liter glass round bottom flask fitted with a mechanical stirring system, a water condenser and a dropping funnel containing the preparation produced in a), and after purging with

argon, the preparation produced in a) is added over 2

hours to 0.18 moles of tetramethoxysilane in the form

of a solution in 400 ml of diethyl ether at ambient

temperature. A heat release takes place and a

5 precipitate appears. When the addition is finished the

mixture is stirred for 30 minutes and then heated to

reflux for 4 hours. The mixture is then cooled to

ambient temperature, the solid being removed by

filtration and washed with ether, still under argon

10 atmosphere. The ether is removed in the rotary

evaporator at approximately 25°C at a pressure of

30 mbar. The residue contains a

dimethoxysilacycloalkane of formula

$$\text{A} \overset{\displaystyle \frown}{\underset{\displaystyle \smile}{}} \text{Si} \underset{\displaystyle OCH_3}{\overset{\displaystyle OCH_3}{<}}$$
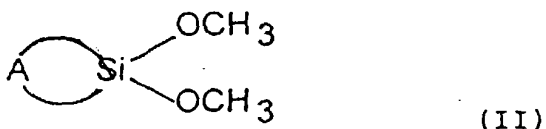
(II)

15 Table 2 gives the boiling points (b.p.) at a pressure

P, of the compounds produced, as a function of the

nature of the divalent radicals A employed.

c) <u>Polymerizations in liquid propylene</u>

The following are introduced, in the order

20 shown, into an 8-liter stainless steel reactor fitted

with a stirring system and a temperature control, after

the reactor has been purged with nitrogen: 2.5 l (STP)

of hydrogen, 6 liters of liquid propylene, 30

millimoles of triethylaluminium in the form of a

solution in hexane at a concentration of 1.5 moles/

liter, and then a dimethoxysilacycloalkane as prepared

5   in b), in the form of a solution in hexane at a

concentration of 0.2 moles per liter, so as to conform

to an Al/Si molar ratio shown in Table 2. After

stirring for 10 minutes at ambient temperature 40 mg of

a solid catalytic component prepared as in Example 12

10 of US Patent 5,212,132 are introduced. With the

stirring continued, the temperature of the reactor is

next raised to 70°C over 10 minutes, kept at this

temperature for an hour and then the reactor is cooled

and decompressed. The results are collected in Table 2.

15   Example 16 (comparative)

Propylene is polymerized in conditions which

are equivalent to those described in c) of the

preceding examples, except that no

alkoxysilacycloalkane is introduced into the

20 polymerization environment. The results are collected

in Table 2.

24

Example No.	Nature of A	Nature of the dimethoxysilacycloalkane obtained	B.p. (°C)	P (mbar)	Al/si	Yield (g/g)	HI (weight %)
		PREPARATION OF ALKOXYSILACYCLOALKANES				POLYMERIZATIONS	
1	tetramethylene	1,1-dimethoxysilacyclopentane	63	40	10	8 100	61.7
2	1-methyltetramethylene	1,1-dimethoxy-2-methylsilacyclopentane	80	33	10	20 640	91.3
3	1-ethyltetramethylene	1,1-dimethoxy-2-ethylsilacyclopentane	92	40	10	30 240	96.2
4	1-n-propyltetramethylene	1,1-dimethoxy-2-n-propylsilacyclopentane	104	40	10	24 300	95.1
5	1-isopropyltetramethylene	1,1-dimethoxy-2-isopropylsilacyclopentane	95-100	1.3	23	36 800	94.1
6	1-n-butyltetramethylene	1,1-dimethoxy-2-n-butylsilacyclopentane	49-51	5.3	10	27 600	94.5
7	pentamethylene	1,1-dimethoxysilacyclohexane	171	1013	10	10 400	82.3
8	1-methylpentamethylene	1,1-dimethoxy-2-methylsilacyclohexane	75-78	40	20	35 100	96.4
9	1-ethylpentamethylene	1,1-dimethoxy-2-ethylsilacyclohexane	102-105	40	20	42 780	97.9
10	1-n-propylpentamethylene	1,1-dimethoxy-2-n-propylsilacyclohexane	88-90	10.7	20	34 200	96.8
11	1-isopropylpentamethylene	1,1-dimethoxy-2-isopropylsilacyclohexane	110-115	40	20	29 800	96.5
12	1-n-butylpentamethylene	1,1-dimethoxy-2-n-butylsilacyclohexane	60-62	4			
13	2,3-dimethyltetramethylene	1,1-dimethoxy-3,4-dimethylsilacyclopentane	68-71	40	10	17 600	89.3
14	1,4-dimethyltetramethylene	1,1-dimethoxy-2,5-dimethylsilacyclopentane	70	40	10	27 700	96
15	hexamethylene	1,1-dimethoxysilacycloheptane	80	40			
16 (comp.)	-	-				7 400	60

TABLE 2

The dialkoxysilacyclohexane used in specific aspects of the present invention may be prepared by a process comprising a step A of reaction between an alkylenedimagnesium dibromide of formula
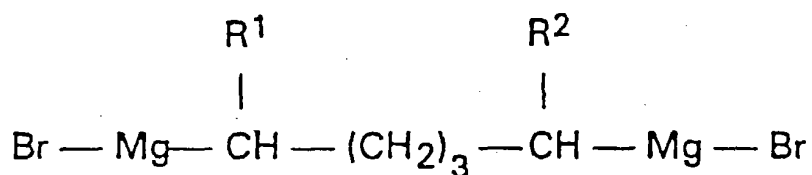
$$\underset{\displaystyle Br-Mg-CH-(CH_2)_3-CH-Mg-Br}{\overset{\displaystyle R^1 \qquad\qquad\qquad R^2}{\overset{\displaystyle | \qquad\qquad\qquad\quad\; |}{}}}$$
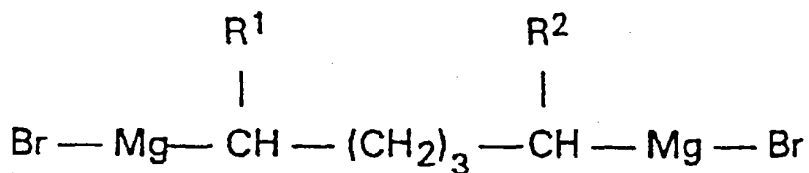
where R^1 and R^2 are as defined above, with a tetraalkoxysilane of formula $(OR^a)(OR^b)(OR^c)(OR^d)Si$, in which R^a, R^b, R^c and R^d are selected from the same group as X and Y, at least one of the radicals R^a, R^b, R^c and R^d being identical to X, and at least one of the radicals R^a, R^b, R^c and R^d being identical to Y. Preferably, X and Y are identical, and in that case, preferably, R^a, R^b, R^c and R^d are also both identical to X and Y.

For the reaction of this stage A, it is possible, for example, to deploy the reactants such

that the molar ratio of the alkylenedimagnesium
dibromide to the tetraalkoxysilane is preferably from 1
to 3.

This reaction is preferably carried out in
5   the presence of a solvent, which may be an ether such
as diethyl ether or tetrahydrofuran (THF), it being
possible for the said solvent to be introduced in an
amount such that the total magnesium concentration
during the entire reaction is preferably between 0.05
10 and 1.2 mol per liter. Before the reaction, the
reactants may be dissolved, separately, in the solvent
and introduced in this form, in solution, into the
reaction medium. For example, before carrying out
reaction, the alkylenedimagnesium dibromide may be in
15 solution in the solvent in an amount of from 0.1 to 1.2
mol per liter, and the tetraalkoxysilane may be in
solution in the solvent in an amount of 0.1 mol per
litre. This reaction may be conducted, for example, at
between 30 and 70°C, although the boiling point of the
20 solvent may constitute an upper temperature limit if
the reaction is conducted at atmospheric pressure.

By way of example, Table 1 below indicates a
number of dialkoxysilacyclohexanes which can be
prepared by reacting tetramethoxysilane with the
25 alkylenedimagnesium dibromide of formula

$$\text{Br} - \text{Mg} - \overset{\overset{\displaystyle R^1}{|}}{\text{CH}} - (\text{CH}_2)_3 - \overset{\overset{\displaystyle R^2}{|}}{\text{CH}} - \text{Mg} - \text{Br}$$

as a function of the nature of R^1 and R^2:

R^1	R^2	Dialkoxysilacyclohexane formed
methyl	methyl	1,1-dimethoxy-2,6-dimethylsilacyclo-hexane,
ethyl	ethyl	1,1-dimethoxy-2,6-diethylsilacyclo-hexane,
n-propyl	n-propyl	1,1-dimethoxy-2,6-di-n-propylsilacyclo-hexane,
isopropyl	isopropyl	1,1-dimethoxy-2,6-diisopropylsilacyclo-hexane,
n-butyl	n-butyl	1,1-dimethoxy-2,6-di-n-butylsilacyclo-hexane,
methyl	ethyl	1,1-dimethoxy-2-ethyl-6-methylsila-cyclohexane,
ethyl	n-propyl	1,1-dimethoxy-2-ethyl-6-n-propylsila-cyclohexane,
ethyl	isopropyl	1,1-dimethoxy-2-ethyl-6-isopropylsila-cyclohexane
ethyl	n-butyl	1,1-dimethoxy-2-n-butyl-6-ethylsila-cyclohexane

5   By way of example, Table 2 below indicates a number of dialkoxysilacyclohexanes which may be

prepared by reacting tetraethoxysilane with the

alkylenedimagnesium dibromide of formula

$$Br-Mg-\underset{\underset{R^1}{|}}{CH}-(CH_2)_3-\underset{\underset{R^2}{|}}{CH}-Mg-Br ,$$
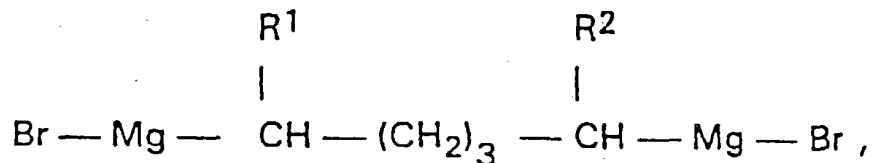
as a function of the nature of R^1 and R^2:

5

R^1	R^2	Dialkoxysilacyclohexane formed
methyl	methyl	1,1-diethoxy-2,6-dimethylsilacyclo-hexane,
ethyl	ethyl	1,1-diethoxy-2,6-diethylsilacyclo-hexane,
n-propyl	n-propyl	1,1-diethoxy-2,6-di-n-propylsilacyclo-hexane,
isopropyl	isopropyl	1,1-diethoxy-2,6-diisopropylsilacyclo-hexane,
n-butyl	n-butyl	1,1-diethoxy-2,6-di-n-butylsilacyclo-hexane,
methyl	ethyl	1,1-diethoxy-2-ethyl-6-methylsilacyclo-hexane,
ethyl	n-propyl	1,1-diethoxy-2-ethyl-6-n-propylsila-cyclohexane,
ethyl	isopropyl	1,1-diethoxy-2-ethyl-6-isopropylsila-cyclohexane
ethyl	n-butyl	1,1-diethoxy-2-n-butyl-6-ethylsila-cyclohexane

The reaction between the alkylenedimagnesium dibromide and the tetraalkoxysilane brings about the formation of BrMgOZ, in which Z is a radical forming part of the group of radicals R^a, R^b, R^c and R^d.

5   This BrMgOZ, which is considered to be a by-product in the context of the present invention, is generally solid and in this case can be removed, for example, by filtration. Following evaporation of the solvent used, the alkoxysilacycloalkane may be purified

10 by distillation, preferably under reduced pressure, for example between 1 and 1×10^3 mbar.

The alkylenedimagnesium dibromide may be prepared, for example, in a step B, by reacting a dibromoalkane of formula

$$Br - \underset{\underset{R^1}{|}}{CH} - (CH_2)_3 - \underset{\underset{R^2}{|}}{CH} - Br \ ,$$

15
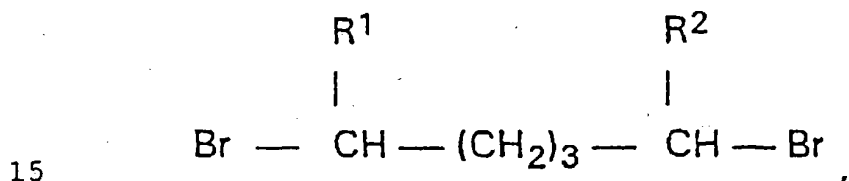
(in which R^1 and R^2 are as defined above) with magnesium, generally in the form of powder or turnings, in the presence of a solvent, for example an ether such as diethyl ether, at for example between 0 and 50°C,

20 under pressure if appropriate - if the volatility of the species employed necessitates it, taking account of the selected temperature.

For the reaction of this step B, the reactants may be deployed with a molar ratio of the

25 magnesium to dibromoalkane ranging preferably from 2 to

2.5, and the amount of solvent may be such that at the beginning of the reaction the dibromoalkane deployed is in a concentration ranging from 0.8 to 1.2 mol per liter of reaction medium. At the end of the reaction,

5   it is recommended to leave the alkylenedimagnesium dibromide in solution at a concentration of more than 0.1 mol per liter, for example between 0.1 and 1.2 mol per liter, and not to attempt to isolate the alkylenedimagnesium dibromide.

10   The dibromoalkane of formula

$$Br - \overset{\overset{\textstyle R^1}{|}}{CH} - (CH_2)_3 - \overset{\overset{\textstyle R^2}{|}}{CH} - Br$$
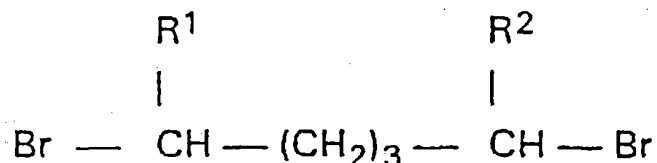
in which R^1 and R^2 are as defined above may be prepared, for example, by a first step of forming a phosphite by reacting a diol of formula

$$HO - \overset{\overset{\textstyle R^1}{|}}{CH} - (CH_2)_3 - \overset{\overset{\textstyle R^2}{|}}{CH} - OH$$
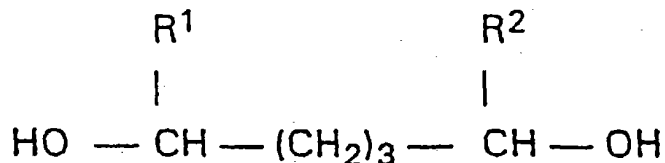
15

with phosphorus tribromide, PBr_3, preferably in the absence of a solvent, under conditions which allow the reaction to be controlled and to be maintained preferably at between 40 and 70°C, in accordance with

20   the following scheme:
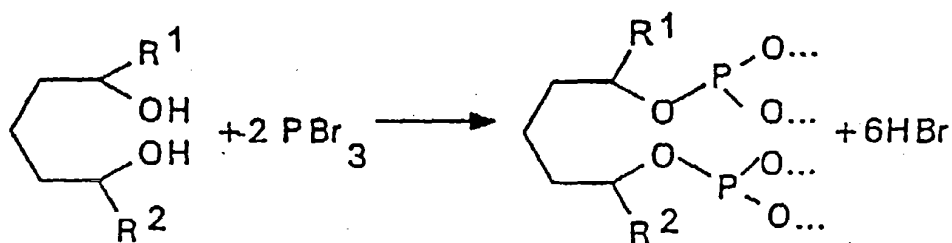
For this reaction between the diol and the PBr$_3$, the reactants may be deployed with a PBr$_3$/diol molar ratio ranging preferably from 2 to 3.

5   In a second step, the phosphite thus formed undergoes conversion to the dibromoalkane, the degree of conversion increasing in proportion to the HBr content of the medium. Consequently, although the medium already contains HBr originating from the

10   reaction forming the phosphite, it is recommended, in a first phase, to add HBr to the medium, for example in an amount such that the molar ratio of the HBr added to the starting diol is from 2 to 3. By this means the medium becomes enriched in dibromoalkane and in P(OH)$_3$.

15   Until the dibromoalkane has formed, the medium is preferably maintained at between 40 and 70°C. It is preferred to wait until the reaction of the first step is already greatly advanced (which can be perceived, for example, by the substantial weakening or even

20   disappearance of the -OH infrared bands) before accelerating the second step by introducing additional HBr.

When the reaction is finished, the medium may be subjected to hydrolysis by adding a volume of water

corresponding, for example, to from 3 to 5 times the

volume of the reaction medium, followed by extraction

with a hydrocarbon such as hexane, cyclohexane or

pentane. Following decantation, the organic phase is

5 separated off and neutralized with a base (for example,

$NaHCO_3$ or Na_2CO_3 or $KHCO_3$) so as to obtain a pH ranging

preferably from 7 to 8. Subsequently, the organic phase

is preferably dried, for example using an anhydrous

salt capable of becoming hydrated (for example, $MgSO_4$ or

10 Na_2SO_4). Following filtration, the solvent may be

evaporated and then the dibromoalkane may be isolated

by distillation.

The diol may be prepared, for example, by

reducing a diketone of the formula

$$O = C - (CH_2)_3 - C = O$$

with R^1 and R^2 substituents as shown.

15 in which R^1 and R^2 are as
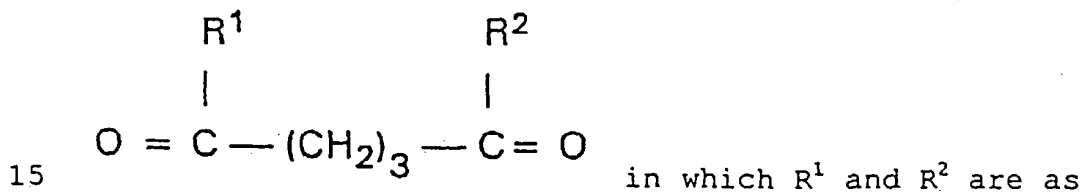
defined above by means of an excess of a reducing agent

such as, for example, $[(CH_3OCH_2CH_2O)_2AlH_2]Na$ or $LiAlH_4$ or

$NaBH_4$, preferably in the presence of an organic solvent,

which may be an aromatic hydrocarbon such as toluene or

20 an ether such as THF or diethyl ether.

The nature of the solvent may be selected as

a function of its suitability for solubilizing the

reducing agent. Preferably, the solvent is present at

least in an amount sufficient to provide complete

25 solubilization of all of the species of the medium. The

maximum amount of solvent may preferably be such that the amount of diketone introduced at the start is up to 1×10^{-2} mol per liter in the reaction medium. For this reaction, the reagents may be introduced such that the

5   reducing agent provides an excess of reductive functions, for example an excess of from 50 to 150% of reductive functions, relative to the ketone functions to be reduced on the diketone. This reduction reaction may be conducted, for example, at from 10°C to 50°C,

10 although the boiling point of the solvent may constitute an upper temperature limit if the reaction is conducted at atmospheric pressure. Following this reaction, the excess reducing agent is decomposed using a base such as aqueous sodium hydroxide solution,

15 containing for example 5% of NaOH (exercising care with regard to the exothermicity of this decomposition). The organic phase is then separated off and treated with carbon dioxide in order to precipitate the dissolved salts it contains. These salts are removed by

20 filtration.

Finally, the diol may be isolated by evaporation from the solvent, followed, if appropriate, by one or more recrystallizations from a hydrocarbon solvent such as cyclohexane.

25 Where R^1 is identical to R^2, the diketone may, for example, be prepared by reacting glutaryl dichloride with an organocuprate of the formula

$$R_2^1 CuM$$
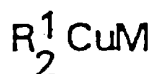
in which R^1 is as defined above and M represents MgBr or MgCl or MgI or Li. This reaction is preferably carried out under an inert atmosphere, such as under nitrogen

5 or argon, and at a temperature of less than or equal to $-45°C$, for example ranging from $-78°C$ to $-45°C$.

This reaction may be conducted preferably such that the molar ratio of the organocuprate to the glutaryl dichloride is from 1.5 to 4. Preferably, this

10 reaction is conducted in the presence of a solvent, which may be a diethyl ether/THF mixture formed from equal volumes of these two solvents. The amount of solvent may be such that, at the beginning of the reaction, the concentration of the organocuprate is

15 between 5×10^{-2} and 1 mol per liter. Following reaction, the mixture may be hydrolysed, for example by means of saturated aqueous NH_4Cl solution, and then extracted with an organic solvent such as diethyl ether. The organic phase may then be washed with 1 N aqueous

20 ammonia until the copper salts are removed, which is recognized by the disappearance of the blue colouration of the ammoniacal solutions of cupric complexes. Finally, following separation of the organic phase, the diketone may be isolated by evaporation of the solvent.

25 The organic cuprate, if it is of formula

$$R_2^1 CuMgBr$$

,

may be prepared, for example, by reacting an
alkylmagnesium compound with cuprous bromide, thus:

$$2R^1 MgBr + CuBr \longrightarrow R^1_2 CuMgBr$$,
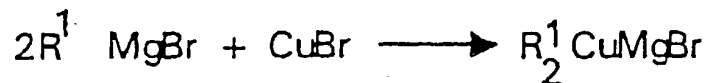
For this reaction, the reagents are
5 preferably introduced in a molar ratio of the
alkylmagnesium compound to the cuprous bromide of
between 1.9 and 2.1. For this reaction, a mixture of
equal volumes of THF and diethyl ether is preferably
present, for example in an amount such that, at the
10 beginning of the reaction, the cuprous bromide is
introduced in an amount of from 5×10^{-2} to 1 mol per
liter. The reaction may be conducted at between $-78°C$
and $-45°C$.

Where R^1 is an ethyl radical, the reaction is
15 preferably carried out in the presence of lithium
chloride.

Preferably, the lithium chloride is
introduced in an amount which is substantially equal to
the amount of alkylmagnesium compound introduced.

20 When R^1 is a radical other than the ethyl
radical, it is likewise possible to use the method
described in "Synthetic Procedures involving
organocopper Reagents", B.H. Lipshutz, p. 283, in
Organometallics in Synthesis, M. Schlosser, Ed., John
25 WILEY and Sons, Chichester, New York, Brisbane,
Toronto, Singapore, 1994.

In the case of asymmetric diketones, where R^1 is different from R^2, the method used is that recommended by K. ABE; H. OKAMURA, T. TSUGOSHI, N. NAKAMURA; Synthesis, 1998, 231.

5   In the examples below, the amount of heptane insolubles (represented by "HI") was measured by extraction of the polymer from the soluble fraction using boiling heptane for two hours in a Kumagawa-type apparatus.

10   **EXAMPLE** 17

1.   Preparation of a solution of ethylmagnesium bromide in diethyl ether.

A 500-ml four-necked flask equipped with a condenser, a mechanical stirrer, a thermometer and an

15   isobaric dropping funnel is charged under nitrogen atmosphere with 5.70 g (235 mmol; 1.1 eq.) of magnesium turnings, which are covered with 15 ml of anhydrous diethyl ether. A few drops of pure ethyl bromide are added in order to initiate the reaction, and then the

20   remaining ethyl bromide is added dropwise (in all 23.23 g; 213 mmol; 1 eq.) in solution in 200 ml of anhydrous diethyl ether. During this addition, the reaction mixture is maintained at a temperature in the region of 5°C. When the addition is finished, it is

25   left with stirring at ambient temperature for four hours until the magnesium turnings have almost completely disappeared.

2.   Preparation of a solution of magnesium diethylcuprate bromide in a mixture of THF and diethyl ether.

A one-liter four-necked flask equipped with a
5 mechanical stirrer, a low-temperature thermometer and an isobaric dropping funnel is charged under nitrogen atmosphere with 13.77 g; (96 mmol; 1 eq.) of CuBr and 8.14 g (192 mmol; 2 eq.) of LiCl in 240 ml of anhydrous tetrahydrofuran (THF) with vigorous stirring at 20°C.
10 After 5 minutes of stirring at 20°C, the solution is cooled to -50°C and then the solution of ethylmagnesium bromide prepared beforehand (192 mmol; 2 eq.) is added dropwise at -50°C. At the beginning of the addition, the solution takes on a green coloration, indicating
15 the formation of the cuprous intermediate, then gradually darkens before becoming violet, which is the colour of magnesium diethylcuprate bromide in this medium. The solution is maintained with stirring at -50°C for 2 hours and is then cooled to -78°C.
20   3.   Preparation of 3,7-nonanedione

8.11 g (48 mmol; 1 eq.) of pure glutaral dichloride are added dropwise at -78°C to the solution of magnesium diethylcuprate bromide obtained above (96 mmol; 2 eq.). When the addition is finished, the
25 temperature of the reaction mixture is slowly (over 1 hour) brought to -45°C. Stirring is maintained at -45°C for 2.5 h.

The mixture is hydrolysed with 200 ml of saturated NH₄Cl solution and then filtered over Celite. The aqueous phase is separated from the organic phase and is then extracted with 3 times 150 ml of ether. The

5 organic extracts are combined and washed with 1 N aqueous ammonia until the blue coloration disappears completely. The organic phase is then washed with 50 ml of water and dried over MgSO₄ and the solvent is evaporated. This gives 7.2 g of 3,7-nonanedione.

10 **4. Preparation of 3,7-nonanediol**

A one-liter four-necked flask equipped with a magnetic stirrer, an isobaric dropping funnel and a thermometer is charged under nitrogen with 27 ml (90 mmol; 2 eq) of the commercial solution "Red-Al"

15 (65% solution of [(MeOCH₂CH₂O)₂AlH₂]Na in toluene) diluted in 200 ml of anhydrous toluene. 3,7-Nonanedione (7 g; 45 mmol; 1 eq.) is dissolved in 260 ml of anhydrous toluene and then added dropwise to the Red-Al solution at room temperature for a period of

20 approximately one hour. The solution is left with stirring at room temperature for one hour more.

After cooling using an ice bath, 15.5 ml of 5% aqueous NaOH solution are added to the solution with care, because the neutralization of the excess Red-Al

25 is highly exothermic. The neutralization is monitored by the intensity of the evolution of hydrogen. Stirring is then stopped and the aqueous phase (loaded with

aluminium hydroxide) decants to the bottom of the
flask. The aqueous phase is separated from the organic
phase. The organic phase is then poured into 100 ml of
toluene containing a piece of dry ice. In the course of

5 stirring, a saline precipitate is observed. The organic
phase is heated at reflux until evolution of CO_2 stops,
and is then filtered. The precipitate is washed with 2
times 5 ml of toluene. The organic extracts are
combined and the solvent is evaporated on a rotary

10 evaporator.

The 3,7-nonanediol is purified by
recrystallization from cyclohexane. Its characteristics
are as follows:
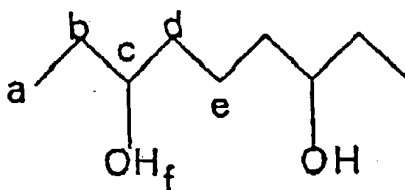
15 Melting point: 43°C

Infrared (cm^{-1}): v(OH): wide band between 3100 and 3700

^{1}H NMR (ppm)/$CDCl_3$ (250 MHz):

Ha: 0.90 t (6H) $^{3}J_{Ha-Hb}$ = 7.0 Hz

Hb + Hd + He: 1.30 - 1.65 m(10 H)

20 Hf: 2.00 - 2.10 m broad (2H)

Hc: 3.50 (2H)

^{13}C NMR (ppm)/$CDCl_3$ (62 MHz): the formation of
two diastereoisomers, threo and meso, is easily
indicated by the presence of two types of carbons b, c,

25 d and e.

1st diastereoisomer: Ca: 9.9

Ce: 21.5

Cb: 30.1

Cd: 36.5

5 Cc: 72.9

2nd diastereoisomer: Ca: 9.9

Ce: 21.7

Cb: 30.2

Cd: 36.7

10 Cc: 73.1

5. Preparation of 3,7-dibromononane

A 100-ml four-necked flask equipped with a thermometer, a magnetic stirrer and an isobaric dropping funnel is charged under nitrogen with 5.62 g

15 (35 mmol; 1 eq.) of 3,7-nonanediol. 7.3 ml (77 mmol; 2.2 eq.) of PBr_3 are then added dropwise at room temperature. The reaction is exothermic and the reaction mixture heats up to 30-35°C then falls back to room temperature. The mixture is then heated at 60°C

20 for 4 hours and is left with stirring at room temperature for 15 hours.

It is subsequently heated to 60°C for 5 hours, during which hydrobromic acid HBr is bubbled in.

25 The reaction mixture is poured onto 50 g of ice and then the organic phase is separated from the aqueous phase. The aqueous phase is extracted with

3 times 20 ml of hexane. The organic extracts are combined and washed with saturated $NaHCO_3$ solution until a pH of more than 7 is obtained and then with 20 ml of water. The organic phase is dried over $MgSO_4$ and the solvent is evaporated on a rotary evaporator. The 3,7-dibromononane is purified by distillation under reduced pressure (boiling at 76-82°C under 0.3 mmHg).

6.   **Preparation of a solution of nonylmagnesium 3,7-dibromide in diethyl ether**

A 100-ml four-necked flask equipped with a condenser, a mechanical stirrer, a thermometer and an isobaric dropping funnel is charged under nitrogen with 1.16 g (48 mmol; 2.25 eq.) of magnesium powder which is just covered with anhydrous diethyl ether. In order to activate the magnesium, a few drops of pure 1,2-dibromoethane and pure 3,7-dibromononane are added. When the reaction has started (start can easily be determined by a positive test using Michler's ketone), 6.05 g (21 mmol; 1 eq.) of 3,7-dibromononane diluted in 20 ml of anhydrous diethyl ether are added dropwise immediately without any cooling of the reaction medium. The mixture is left with stirring at room temperature for 4 h after the end of the addition.

7.   **Preparation of 1,1-dimethoxy-2,6-diethylsila-cyclohexane**

A 250-ml four-necked flask equipped with a condenser, a magnetic stirrer, a thermometer and an

isobaric dropping funnel is charged under nitrogen with

2.91 g (19.2 mmol; 0.9 eq.) of tetramethoxysilane in

20 ml of anhydrous diethyl ether. This is followed by

the dropwise addition at room temperature of the

5   ethereal solution of nonylmagnesium 3,7-dibromide,

prepared beforehand, and then the solution is brought

to reflux for 4 hours.

The mixture obtained is filtered under

nitrogen and then centrifuged in order to remove some

10   of the magnesium salts formed. The ether is

subsequently evaporated on a rotary evaporator at 30°C.

Then 10 ml of ether are added and the solution is then

stirred and centrifuged, for the purpose of completely

removing the residual magnesium salts. The supernatant

15   liquid obtained is subsequently subjected to a first

rapid distillation under partial vacuum (0.3 mm Hg),

the distillate being trapped in a tube immersed in

liquid nitrogen. It is noted that a first fraction

distils at about 28°C and that the remainder distils at

20   between 40°C and 120°C without observing a fixed point.

The fraction which has distilled at about 28°C

essentially comprises one or more secondary elimination

products containing at least one ethylenic double bond.

The other fraction is redistilled under reduced

25   pressure (2×10^{-2} mm Hg) with a microdistillation

assembly, the various fractions being trapped in tubes

immersed in liquid nitrogen. The following three

fractions are obtained:

fraction 1:   42-48°C,

fraction 2:   50-57°C,

5   fraction 3:   58-104°C.

        Fractions 1 and 2 are mixtures containing

approximately 95% of the threo and meso

diastereoisomers of 2,6-diethyl-1,1-dimethoxysila-

cyclohexane. Fraction 1 (480 mg) is a 91/9 threo/meso

10 mixture (determined by gas chromatography). Fraction 2

(940 mg) is an 82/12 threo/meso mixture (determined by

gas chromatography). The NMR characteristics of the

majority, threo stereoisomer of 2,6-diethyl-1,1-

dimethoxysilacyclohexane, as determined from fraction

15 1, are as follows:
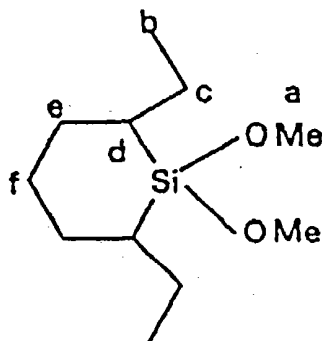
^{1}H NMR (ppm)/CDCl$_3$ (250 MHz):

        Hd: 0.70-0.90 m (2H)

        Hb: 0.90 t (6H) $^3J_{Hb-Hc}$ = 7.5 Hz

20   Hc: 1.20-1.35 and 1.50-1.65 two multiplets (4H)

        Hf: 1.35-1.45 m (2H)

        He: 1.50-1.60 and 1.70-1.75 two multiplets (4H)

        Ha: 3.55 s (6H)

^{13}C NMR (ppm)/CDCl$_3$ (62 MHz)

Cb: 13.3

Cc: 21.6

Cf: 23.2

5   Cd: 24.7

Ce: 30.1

Ca: 50.6

EXAMPLE 18

A 3.6-liter stainless steel reactor equipped

10 with a stirrer system and a temperature regulator is

first purged with nitrogen and then charged with 5.7 l

(S.T.P.) of hydrogen, then 2.4 litres of liquid

propylene, then 30 millimol of triethylaluminium in the

form of a 1.5 mol/liter solution in hexane, then

15 1.5 millimol of 1,1-dimethoxy-2,6-diethylsilacyclo-

hexane in the form of a 0.2 mol per liter solution in

hexane (giving an Al/Si molar ratio of 20).

Subsequently, with stirring, 40 mg of a solid catalytic

component prepared as in Example 12 of the Patent

20 US 5,212,132 are introduced, after which the

temperature of the reactor is raised to 70°C over 10

minutes and held at this temperature for one hour. The

reactor is subsequently cooled and decompressed. A

polypropylene having a heptane insolubility index of

25 98.8 was obtained with a productivity of 52,000 g of

polymer per g of solid catalytic component.

EXAMPLE [19] (comparative)

The procedure of Example 2 is repeated except that the 1,1-dimethoxy-2,6-diethylsilacyclohexane is replaced by the same number of moles of 1,1-dimethoxy-

5 2-ethylsilacyclohexane.

A polypropylene having a heptane insolubility index of 97.9 was obtained with a productivity of 40,000 g of polymer per g of solid catalytic component.

Although the invention has been described in conjunction with specific embodiments, it is evident that many alternatives and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, the invention is intended to embrace all of the alternatives and variations that fall within the spirit and scope of the appended claims. The above references are hereby incorporated.